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Uranium and Plutonium Solution Assays by Transmission-Corrected X-Ray Fluorescence

Richard W. Ryon and Wayne D. Ruhter
Lawrence Livermore National Laboratory
Livermore, CA 94550

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URANIUM AND PLUTONIUM SOLUTION ASSAYS
by
TRANSMISSION-CORRECTED X-RAY FLUORESCENCE

Richard W. Ryon and Wayne D. Ruhter
Lawrence Livermore National Laboratory
Livermore, California 94551 USA

Abstract:

We have developed an x-ray fluorescence analysis technique for uranium and plutonium solutions which compensates for variations in the absorption of the exciting gamma rays and fluorescent x-rays. We use ^{57}Co to efficiently excite the K lines of the elements, and a mixed ^{57}Co plus ^{153}Gd transmission source to correct for variations in absorption. The absorption correction is a unique feature of our technique which permits accurate calibration with a single solution standard and the measurement of a wide range of concentrations (up to 300 grams per liter). Without this correction procedure, up to six solution standards are required to correct for non-linearity over this concentration range. In addition, other elements present in the specimens and not present in the standards would otherwise reduce the accuracy or even invalidate the analyses.

Specially designed equipment incorporates a planar intrinsic germanium detector, excitation and transmission radioisotopes, and specimen holder. The apparatus can be inserted into a rubber glove of a glovebox, keeping the apparatus outside and the solutions inside the glovebox, thereby protecting the user and the equipment from possible contamination.

This technique will be tested at the Bochvar Institute of Inorganic Materials in Moscow for possible use in the Russian complex of nuclear facilities. This is part of a cooperative program between laboratories in the United States and Russia to strengthen systems of nuclear materials protection, control, and accountability (MPC&A) in both countries. A part of this program is to accurately measure and track inventories of materials, thus the need for good non-destructive analytical techniques.

Background:

With the end of the Cold War, the international community of nations has come to face a common problem: the possibility that special nuclear materials (plutonium and highly enriched uranium) might be diverted to a rogue state or terrorist organization.[1] As little as eight kilograms of these materials is sufficient to build a nuclear weapon. The threat posed is most urgent in Russia and some of the other former Soviet republics. More than half of the weapons-usable material produced by the Soviet Union is in fact in assembled nuclear weapons in Russia. Because weapons are strictly accounted for and heavily guarded at secure military sites, they are considered to be much less vulnerable to theft or diversion than weapons-usable materials in other forms. The greatest threat is therefore posed by the approximately 650 metric tons of weapons-usable materials that exists in forms such as metals, oxides, solutions, and scrap. These materials are in use or storage at close to 50 sites across Russia and other newly independent

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states. The former system which protected these materials (summarized in the phrase “guards, guns, and gulag”) is no longer relevant.

For the above reasons, the United States Department of Energy and its national laboratories have initiated a program of cooperation with the Russian Federation’s nuclear laboratories to strengthen systems of nuclear materials protection, control, and accountability (MPC&A) in both countries. As part of this multi-laboratory program, the Lawrence Livermore National Laboratory (LLNL) and the A.A. Bochvar Research Institute of Inorganic Materials (VNIINM) are collaborating in the study and application of x-ray fluorescence analysis techniques for the nondestructive assay of solutions containing uranium or plutonium.

X-Ray analysis of uranium and plutonium solutions has been investigated and developed at LLNL for a number of years[2,3,4] in conjunction with the reprocessing of spent nuclear fuel. Since the United States no longer has any active plans to reprocess nuclear fuel, the technique has not been implemented and has been held in a standby state for several years. With the advent of the joint U.S. - Russia MPC&A Program, we have reactivated the technique, tested it in a laboratory setting at LLNL, improved the software, and initiated testing at VNIINM.

Equipment and Experimental Considerations:

A schematic diagram of the equipment is shown in Figure 1. Two ^{57}Co sources (2 mCi each) are used to excite fluorescence. A mixed ^{57}Co and ^{153}Gd transmission source (2 mCi each isotope) is finely collimated to pass radiation through the solution cell. A tungsten shutter can be closed, blocking radiation from the exciter from reaching the specimen, and allowing only passive radiation from the specimen and transmitted radiation from the transmission source to reach the detector. All radiation sources are shielded so that no stray radiation reaches the detector. If concentrated plutonium is to be analyzed, a rhodium foil may be inserted between the specimen and detector to attenuate the intense 59.6 keV radiation from ^{241}Am present in aged plutonium. The specimen cell may be any precision bore cylindrical tube, such as glass or stainless steel, with an inside diameter larger than the detector’s collimator.

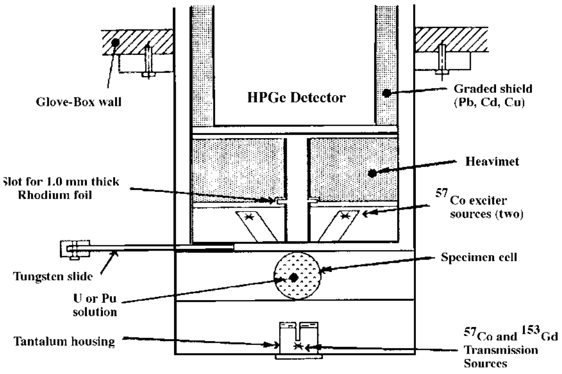

Figure 1. Schematic drawing of one adaptation of the equipment, mounted to the wall of a glovebox. We currently use a system which fits into a rubber glove in the glovebox, and omits the Rh foil.

^{57}Co is an ideal exciter for this application, because its 122.1 keV gamma ray lies just above the absorption edges of uranium and plutonium (115.6 keV and 121.7 keV, respectively). ^{153}Gd is likewise ideal: its 97.4 keV and 103.2 keV gamma rays are close in energy to the Kα1 lines of U and Pu (98.4 keV and 103.7 keV, respectively) and therefore can be used to correct for absorption of the fluorescent lines by the solution. ^{57}Co in the transmission source corrects for the exciter attenuation by the solution, as well as providing lines for energy calibration for each spectrum measured. Nature is again kind to us, as the half-lives for ^{57}Co and ^{153}Gd are similar (270 days and 242 days, respectively).

Results:

Passive and active spectra from a uranium solution are shown in Figure 2. Overlapping peaks are deconvolved using a sophisticated peak shape fitting code that includes a Gaussian function, a Lorentzian profile for x-rays, short-term low-energy tailing, and background continuum.[5] The net intensities for the measured fluorescent x-rays are a non-linear function of concentration. Because an equation for absorption cannot be written for the near-field geometry used here, as can be done for far-field geometry, an explicit correction for absorption of the ^{153}Gd lines is calculated using numerical integration over the cylindrical volume seen by the detector. This correction effectively corrects for solution self-absorption, as seen in Figure 3. The concentration is then calculated simply as

$$\mathrm{Conc}_{\mathrm{meas}} = \mathrm{K} \bullet \mathrm{CF}_{\mathrm{meas}} \bullet \mathrm{Intensity}_{\mathrm{meas}}$$

$$\mathrm{K} = \mathrm{CF}_{\mathrm{std}} \bullet \mathrm{Intensity}_{\mathrm{std}} \div \mathrm{Conc}_{\mathrm{std}}$$

where K is the calibration constant and $\mathrm{CF}_{\mathrm{meas}}$ and $\mathrm{CF}_{\mathrm{std}}$ are the absorption correction factors for the unknown and standard, respectively. When precision-bore cells are used, the calibration constant is very precise (Table 1).[6]

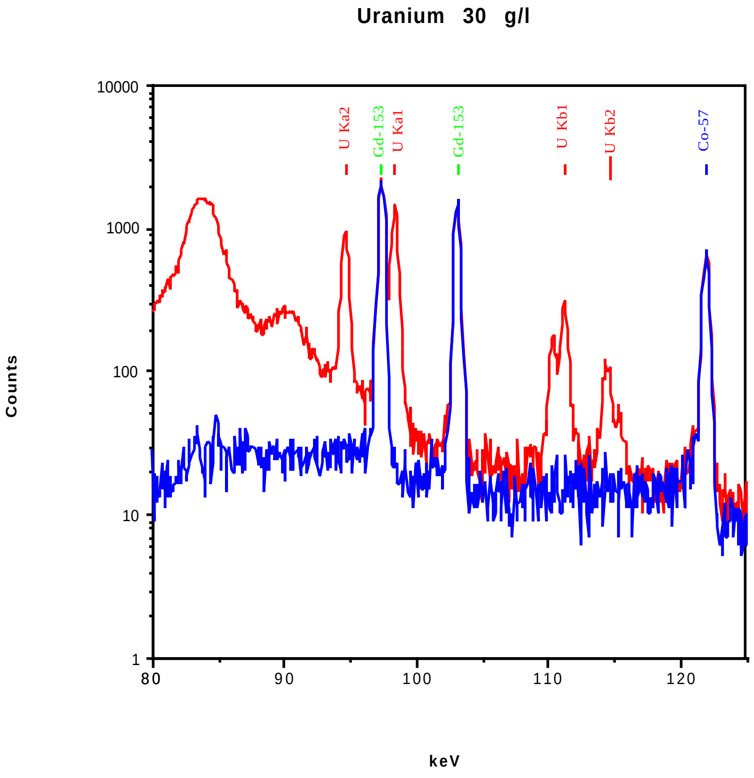

Figure 2. Passive and active spectra from 30 g/l uranium

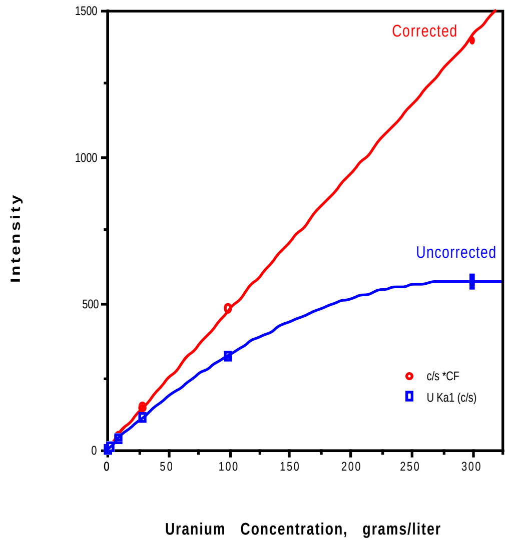

Figure 3. Corrected and Uncorrected U Kα1 intensities

Table 1. Calibration Constants:

Uranium conc., g/l	Calibration Constant	Plutonium conc., g/l	Calibration Constant
240.9	10.662	238.95	14.008
178.8	10.659	178.29	14.074
105.0	10.613	119.54	14.032
52.67	10.584	41.95	13.950
21.23	10.549	19.80	13.988
10.56	10.650	5.158	13.964
5.333	10.645	1.774	14.089
2.143	10.699	0.995	13.992
1.099	10.619		
weighted mean:	10.623 ± 0.42%		14.015 ± 0.40%

Conclusion:

We have developed and demonstrated an x-ray fluorescence technique for the determination of uranium and plutonium concentrations in solutions, applicable over a wide range of concentrations (tested up to 300 g/l). Measurements can be made through barriers, such as rubber gloves in a glovebox or even stainless steel tubing in a reprocessing plant; contamination and waste generation are thereby avoided. The method is relatively fast, 10’s of seconds to minutes. The equipment is relatively simple and inexpensive. Only one solution standard is required, and its matrix need not be identical to the solutions being measured. The absolute accuracy may be as good as 0.5%. The technique is extended to measuring isotopic compositions from the passively observed gamma radiation using an adaptation of the well-know code MGA[7] (not demonstrated here).

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All correspondence should be directed to:

Richard W. Ryon
Isotope Sciences Division L-231
Lawrence Livermore National Laboratory
P.O. Box 808
Livermore, California 94551 USA

Telephone: 925-422-6324

Fax: 925-422-3160

E-mail: ryon2@llnl.gov

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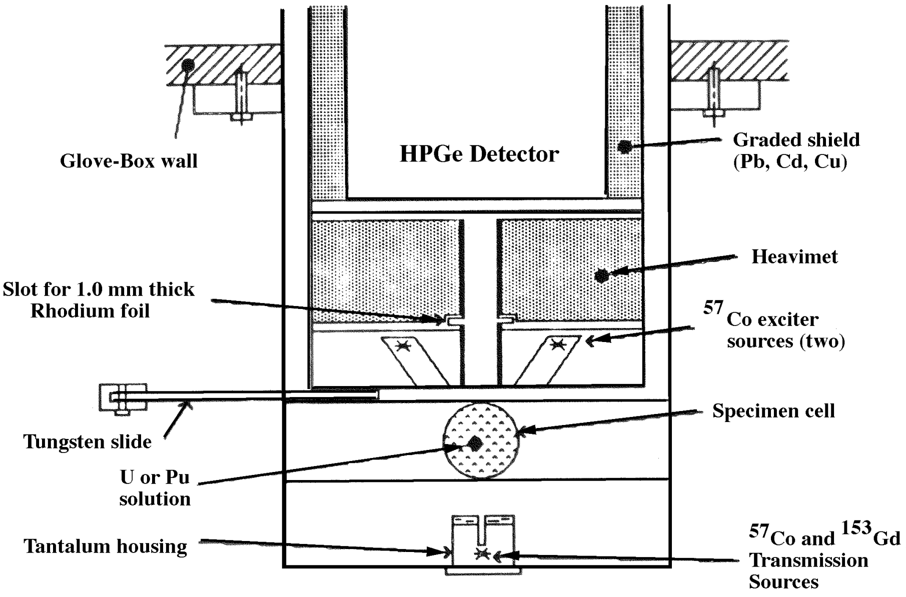

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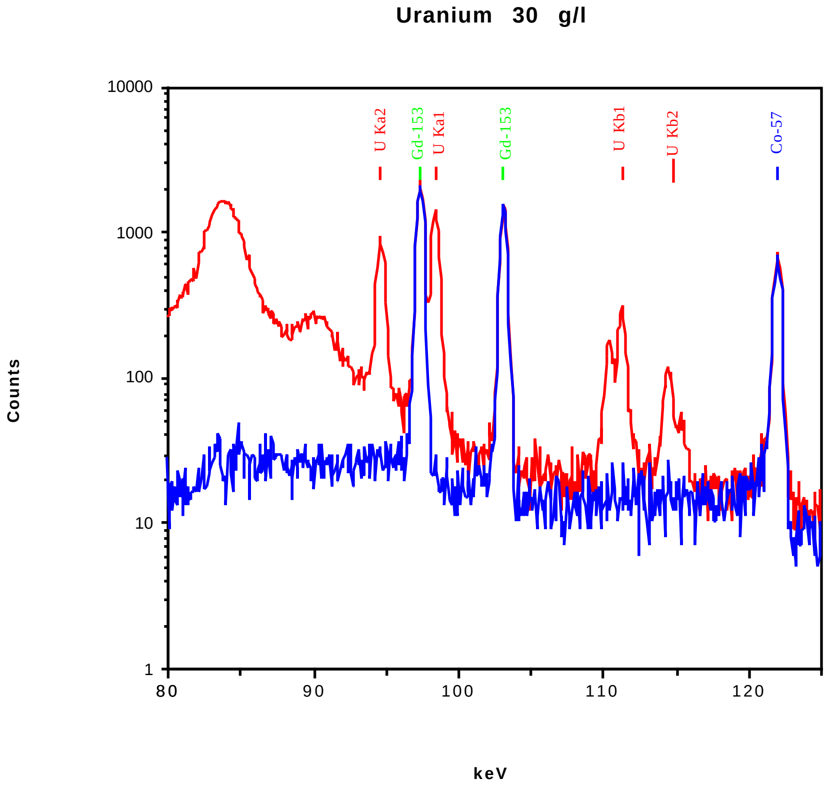

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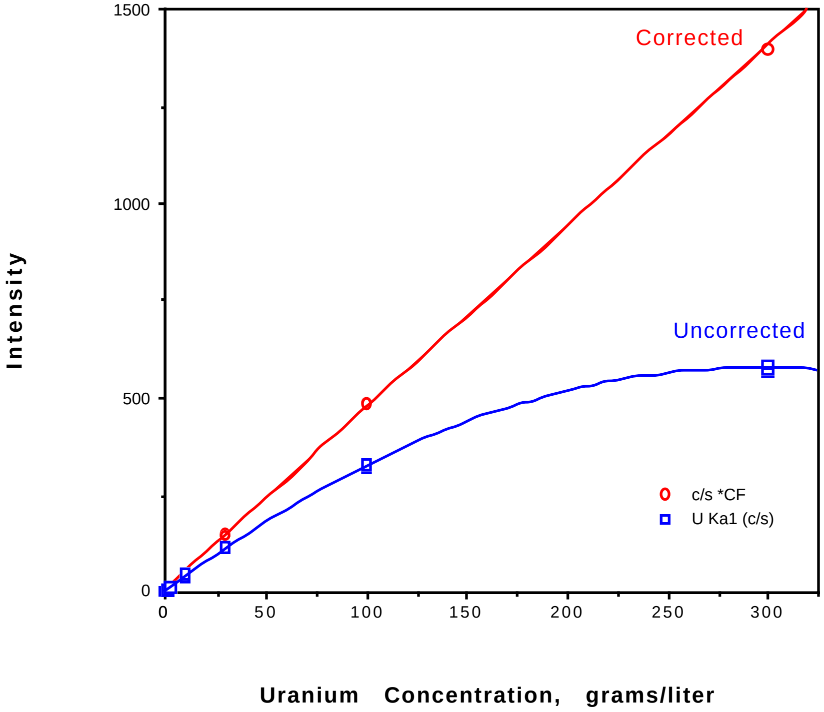

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